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Polymorphism in an Aqua-Bridged, Dinuclear 2-Nitrobenzoate Complex of Cobalt(II)

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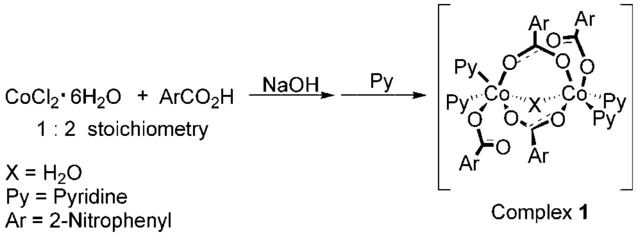
Three polymorphs of a dinuclear, aqua-bridged cobalt complex with the composition $[Co_2(\mu\text{-}OH_2)(C_5H_5N)_4(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NO_2)_2(O_2CC_6H_4\text{-}2\text{-}NO_2)_2]$ are identified and the crystal structures are determined by X-ray crystallography. Selective crystallisation of the polymorphs can be achieved by controlling the reaction conditions as well as the crystallisation processes. The reaction of cobalt(II) acetate tetrahydrate with 2-nitrobenzoic acid followed by treatment with excess pyridine leads to a mononuclear complex with the composition $[Co(H_2O)_2(C_5H_5N)_2(O_2CC_6H_4\text{-}2\text{-}NO_2)_2]$.

Introduction

Polymorphism of a molecule (or compound) may be related to the ability of it having different crystalline phases. The crystallisation process leading to a polymorph is generally sensitive to variation in the conditions of temperature, pressure and/or the manner in which the crystals are obtained.[1] Polymorphism in organic crystals,[2] including crystals of pharmaceutically active compounds,[3] is an active area of research, which is driven by the rationale that such a study would provide insight/understanding into the kinetic and thermodynamic factors that govern nucleation and crystal growth. Subsequently, this may enable us to gain control of the crystallisation process, and in particular, the production/exclusion of the specific polymorph. Studies have shown that interconversion between polymorphs is possible through the mechanochemical processing of solid compounds[4] or through the mixing of several components in the solid phase.[5] Consequently, aspects related to the synthesis, structure and polymorphism in metal coordination complexes is emerging as an active field of research.[6] In this communication, we report three polymorphs of an aqua–bridged, dinuclear cobalt(II) complex **1** and describe their synthetic and structural aspects. From a structural perspective, such aqua-bridged dinuclear cobalt(II) complexes may be regarded as synthetic mimics of the active sites of certain metalloenzymes[7] such as leucine aminopeptidase as they contain a dinuclear cobalt core that has an aqua as well as a carboxylate group as bridged ligands, along with monodentate nitrogen-containing ligands at two ends. This makes their study quite relevant. While the complex itself [having the same coordination environment about the two cobalt(II) ions] may be synthesised by grinding the solid reactants followed by solution processing or by solution processing alone, the polymorphs may be identified from differences in the relative orientation of the 2-nitrobenzoate groups that are coordinated to the cobalt(II) ions in the complex. A similar phenomenon is known for organic compounds,[8] but is less known for coordination complexes of cobalt(II) carboxylate compounds.[9a]

Results and Discussion

We have found that the reaction of cobalt(II) chloride hexahydrate with 2-nitrobenzoic acid, sodium hydroxide and pyridine in methanol gives complex **1** [Equation (1)], which crystallises as pink rods in the triclinic space group $P\bar{1}$ (polymorph **I**).



(1)

In this complex, each cobalt(II) ion is coordinated to a monodentate benzoate molecule and two pyridine molecules; the six-coordinate octahedral geometry is completed by two bridging 2-nitrobenzoate groups and a bridging aqua ligand. The monodentate 2-nitrobenzoate molecule is intramolecularly hydrogen bonded to the bridging aqua group {O(17)–H···O(14) [2.578(2) Å, 167(3)°] and O(17)–

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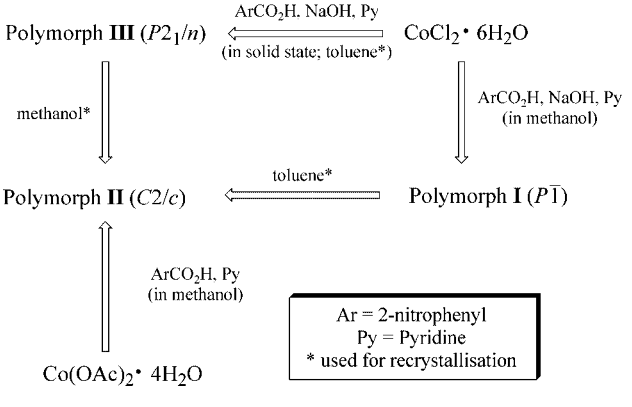
H···O(2) [2.508(3) Å, 177(4)°]}. The corresponding Co(1)–O(17) and Co(2)–O(17) bond lengths are found to be 2.1255(15) and 2.1278(15) Å, respectively, while the Co(1)–O(17)–Co(2) bond angle is 114.55(7)°. Moreover, weak intramolecular C(6)–H···O(3) [3.255(4) Å, 158°], C(6)–H···O(1) [3.103(3) Å, 124°], C(10)–H···O(10) [3.104(4) Å, 125°], C(10)–H···O(12) [3.281(5) Å, 150°] and C(17)–H···O(5) [2.722(3) Å, 101°] interactions are also observed in this polymorph. These interactions stabilise the *out-out* orientation of the nitro groups of 2-nitrobenzoate ligand relative to the Co(1)–O(17)–Co(2) fragment in the complex. These molecules have a self-assembled structure in the lattice through weak C(14)–H···O(12) [3.429(4) Å, 158°] and C(2)–H···O(7) [3.279(5) Å, 139°] interactions, and the corresponding packing diagram is shown in Figure 2a. We have also found two other polymorphs of this compound, and the synthesis of these polymorphs is highly dependent on the reaction conditions, as illustrated in Scheme 1. The crystal structures of all the three polymorphs were determined and are shown in Figure 1.

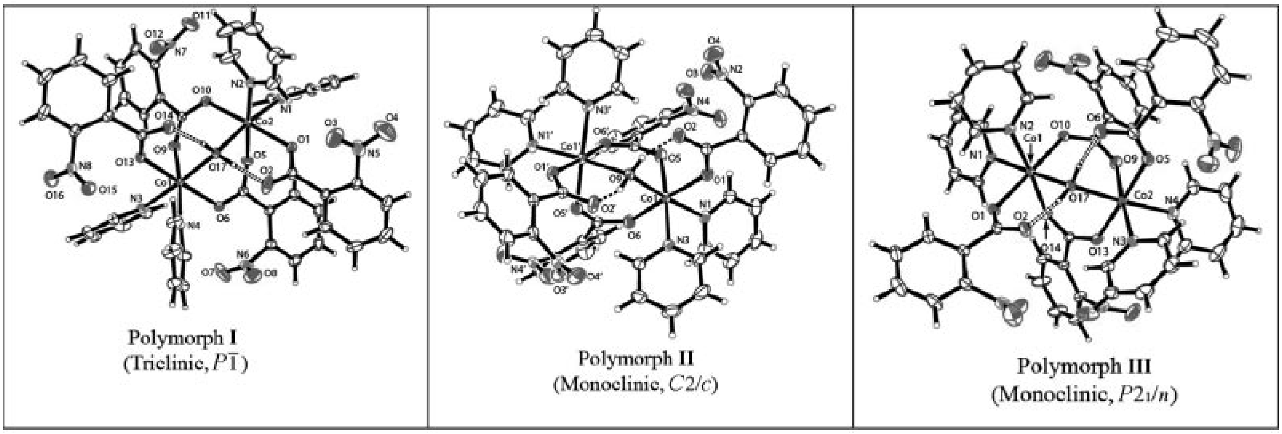


Scheme 1.

Complex **1** was also prepared by reaction of cobalt(II) acetate tetrahydrate with 2-nitrobenzoic acid and pyridine in methanol. However, this complex crystallises, from methanol, as pink plates in the monoclinic *C*2/*c* space group (polymorph **II**). In polymorph **II**, each cobalt(II) ion is coordinated to a monodentate 2-nitrobenzoate molecule and two pyridine molecules; two bridged 2-nitrobenzoate groups and the aqua bridge complete the six-coordinate octahedral geometry. The crystal structure of **II** shows that the complex is stabilised [such that the Co(1)···Co(1′) distance is 3.616(3) Å] by intramolecular hydrogen bonding between the monodentate 2-nitrobenzoate and bridging aqua groups {O(9)–H···O(2) [2.582(16) Å, 157°]}. The corresponding Co(1)···O(9) distance is 2.142(9) Å, while the Co(1)–O(9)–Co(1′) bond angle is 115.11(8)°. The packing structure of **II** is shown in Figure 2b, wherein the molecules are held in the lattice through weak intermolecular C3–H···O2 [3.229(3) Å, 156°] and C4–H···O4 [3.292 Å, 127°] interactions. In polymorph **II**, the nitro groups of each carboxylate ligand projects inwards and they therefore may be described as having *in-in* orientations.

Reaction of cobalt(II) chloride hexahydrate, 2-nitrobenzoic acid and sodium hydroxide in the solid state followed by addition of pyridine (in a 1:2:2 stoichiometry) also gave the dinuclear cobalt(II) complex **1**. This complex is soluble in toluene and could subsequently be crystallised as pink plates in the $P2_1/n$ space group (polymorph **III**). The packing diagram of this polymorph is given in Figure 2c.

It is noteworthy that in polymorph **I**, each of the nitro groups adopts an *out-out* orientation in the dinuclear cobalt(II) complex. On the other hand, polymorph **III** can be identified by two of the 2-nitrobenzoate groups adopting an *out-out* orientation and two adopting an *out-in* orientation relative to the Co–O–Co fragment. The corresponding powder XRD patterns of the polymorphs were recorded and compared with the calculated patterns, which substantiated our observation of distinct crystalline phases. Surprisingly, recrystallisation of polymorph **I** from methanol gave pink "square" plates, and structural analysis led to the identification of polymorph **II** (monoclinic *C*2/*c*). Similarly, recrystallisation experiments of polymorph **III** from toluene also gave pink "square" plates in the *C*2/*c* space group. Subsequently, we performed powder XRD analysis of the samples (see Supporting Information), which confirmed the



Polymorph I (Triclinic, $P\bar{1}$)

Polymorph II (Monoclinic, $C2/c$)

Polymorph III (Monoclinic, $P2_1/n$)

Figure 1. Crystal structures of three dinuclear polymorphs of **1** (30% thermal ellipsoid).

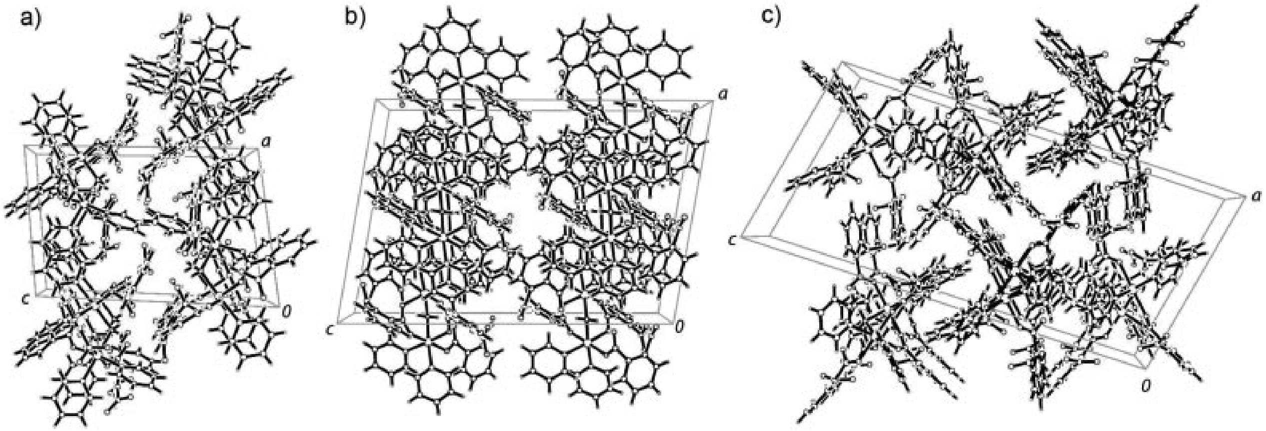


Figure 2. Packing structures of complex **1**: a) polymorph **I**, (b) polymorph **II** and (c) polymorph **III**.

conversion of both polymorphs **I** and **III** into **II**, as illustrated in Scheme 1.

A close inspection of the bond lengths (Table 1) in the three polymorphs of complex **1** shows that the coordination environment around each cobalt(II) ions is similar; the cobalt(II) ions are coordinated to a monodentate benzoate group and two N-donor pyridine ligands. The two cobalt(II) ions are bridged by two 2-nitrobenzoate ligands and an aqua group that is intramolecularly hydrogen bonded to the carboxyl group of the monodentate 2-nitrobenzoate.

Table 1. Selected bond lengths [Å] and angles [°] in **I**–**III**.[a]

	Polymorph **I** ($P\bar{1}$)	Polymorph **II** ($C2/c$)	Polymorph **III** ($P2_1/n$)
Co(1)–O(X)	2.120(1)	2.091(1)	2.127(2)
Co(1)–O(Y)	2.114(1)	2.108(1)	2.086(2)
Co(1)–O(Y′)	2.078(1)	2.075(1)	2.105(1)
Co(2)–O(X)	2.148(1)	2.091(1)[b]	2.122(2)
Co(2)–O(Y)	2.096(1)	2.108(1)[b]	2.063(2)
Co(2)–O(Y′)	2.102(1)	2.075(1)[b]	2.076(2)
Co(1)–N′(#1)	2.147(2)	2.138(1)	2.164(2)
Co(1)–N′′(#2)	2.158(2)	2.147(1)	2.156(2)
Co(2)–N′(#1)	2.151(2)	2.138(1)[b]	2.140(2)
Co(2)–N′(#2)	2.146(2)	2.147(1)[b]	2.162(2)
Co(1)–O(aqua)	2.126(2)	2.142(8)	2.136(2)
Co(2)–O(aqua)	2.128(2)	2.142(8)[b]	2.157(2)
Co(1)···Co(2)	3.578	3.616	3.651
Co(1)–O–Co(2)	114.55(7)	115.12(7)[b]	116.49(7)

[a] X = (2-nitrobenzoate); Y, Y′ = μ-(2-nitrobenzoate). [b] $-x$, y, $-z+1/2$.

Each of the polymorphs (**I**–**III**) described above obtained from complex **1** shows broad signals centred at 3407 cm^{-1} (O–H stretching) in their solid-state FTIR spectra. This apparently corresponds to the presence of intramolecular hydrogen-bonding interactions involving the 2-nitrobenzoate group and the bridging aqua ligand. Solid-state FTIR spectra of polymorphs **II** and **III** exhibit similar absorptions in the carbonyl C=O (1531 and 1635 cm^{-1}, respectively) and nitro N–O stretching regions (1364 and 1395 cm^{-1}, respectively). While the corresponding C=O absorptions of polymorph **I** are similar to those of **II** and **III**, the N–O stretching bands appear as a broad absorption at 1390 cm^{-1} with a shoulder at about 1356 cm^{-1}.

In order to study the influence of the solvent on the crystallisation process, we performed the reaction of the cobalt(II) salts with 2-nitrobenzoic acid and sodium hydroxide in the presence of excess pyridine rather than by using the stoichiometric amount. In each case, two concomitant complexes were obtained both by solid-state synthesis and by solution processing. One of the complexes, which was obtained as orange prisms, turned out to be the mononuclear cobalt(II) complex **IV**, as depicted in Figure 3. The other complex was found to be the dinuclear complex **1** that crystallises as pink rods in the $P\bar{1}$ space group.

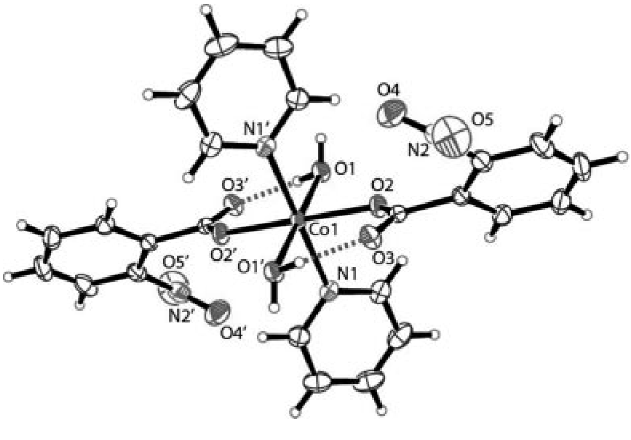


Figure 3. Structure of the mononuclear complex **IV**.

The mononuclear complex **IV** is formed preferentially during the reaction of cobalt(II) sulfate heptahydrate with 2-nitrobenzoic acid in the presence of sodium hydroxide and excess pyridine in methanol. Similarly, reactions of cobalt(II) chloride with 2-nitrobenzoic acid and sodium hydroxide in excess pyridine led to mononuclear complex **IV**, which suggests that the role of anion in the synthesis through the solution route is not prominent. However, the formation of polymorph **I** from the reaction of cobalt chloride with 2-nitrobenzoic acid in the presence of sodium hydroxide and pyridine and the formation of polymorph **II** directly from the reaction of cobalt(II) acetate with 2-nitrobenzoic acid and pyridine clearly indicates that the reaction conditions and the crystallisation procedures can influence the formation and isolation of crystal(s) of the complexes with different orientations of the nitro groups. The polymorphs **I**–**III** isolated in this study are three conformers of several possible conformers that can be envisaged by imagining the dimeric core as a rigid unit and by fixing the 2-nitrophenyl groups in different orientations at two ends of the rigid unit – similar to those for cubane-type organic molecules with different orientations of nitro groups.[8b]

In conclusion, we have shown that depending on the method of synthesis and crystallisation, three distinct polymorphs (**I**–**III**) of an aqua–bridged, dinuclear 2-nitrobenzoate cobalt(II) complex **1** may be obtained. In this case, the formation of polymorphs originates from the orientations of the nitro group in the 2-nitrobenzoate units in the complex. The formation of the polymorphs is controlled by three factors: (a) the synthetic route (solid- or solution phase), (b) the solvent of crystallisation and (c) the stoichiometry of the auxiliary ligand pyridine.

Experimental Section

X-ray crystallographic data were collected at 296 K with a Mo-K_α radiation source (λ = 0.71073 Å) by using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection, for indexing the reflections and for determining the unit cell parameters; the collected data were integrated by using the SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations (F^2) by using the SHELXTL-97 software. All non-H atoms were refined in the anisotropic approximation against F^2 for all reflections. All H atoms, except those attached to O atoms, were placed at their calculated positions and refined in the isotropic approximation; those attached to heteroatoms were located in the difference Fourier maps and refined with isotropic displacement coefficients. Crystal data for the cobalt complexes is given in Table 2. CCDC-619774, CCDC-619773, CCDC-608665 and CCDC-620812 (for compounds **I**–**IV**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Polymorphs I: 2-Nitrobenzoic acid (0.34 g, 2 mmol) was dissolved in methanol (10 mL) and sodium hydroxide (0.081 g, 2 mmol) was added to it. The mixture was stirred vigorously for 5 min, and cobalt(II) chloride hexahydrate (0.238 g, 1 mmol) was then added. The reaction mixture became pink, and subsequently pyridine (0.158 g, 2 mmol) was added. The solution was filtered, and the pink filtrate was kept at room temperature. Pink, rodlike crystals were obtained after 3 d, which were then collected and dried in air. Yield 44 % (based on Co).

Synthesis of Polymorph II: 2-Nitrobenzoic acid (0.34 g, 2 mmol) was added to a solution of cobalt acetate tetrahydrate (0.249 g, 1 mmol) in methanol (20 mL), and the mixture was stirred overnight. To this solution, pyridine (0.158 g, 2 mmol) was added, and the mixture stirred for 10 min. On standing for 2 d, square–shaped, pink crystals were obtained from the reaction mixture. Yield 41 % (based on Co).

Synthesis of Polymorph III: 2-Nitrobenzoic acid (0.34 g, 2 mmol), sodium hydroxide (0.081 g, 2 mmol) and $CoCl_2\cdot 6H_2O$ (0.238 g, 1 mmol) was finely ground with a mortar and pestle and heated at 100 °C for 15 min – the pink colour turns to blue. The reaction mixture was cooled to room temperature and transferred into a

Table 2. Crystal parameters and refinement data for polymorphs **I**–**III** and complex **IV**.

	I	**II**	**III**	**IV**
Formula	$C_{48}H_{38}Co_2N_8O_{17}$	$C_{48}H_{38}Co_2N_8O_{17}$	$C_{48}H_{38}Co_2N_8O_{17}$	$C_{24}H_{22}CoN_4O_{10}$
M_w	1116.72	1116.72	1116.72	585.39
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$
Temperature [K]	296	296	296	296
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	11.8668(2)	16.0312(3)	13.6133(4)	7.2206(5)
b [Å]	13.8387(2)	13.5441(3)	13.3201(4)	8.5518(6)
c [Å]	17.8115(3)	23.7144(5)	28.6728(9)	11.0026(7)
α [°]	68.727(10)	90	90	97.169(1)
β [°]	75.229(10)	99.850(10)	101.746(2)	98.233(1)
γ [°]	66.628(10)	90	90	108.126(1)
V [Å^3]	2480.91(7)	5073.16(18)	5090.4(3)	628.59(7)
Z	2	4	4	1
Density [Mg m^{-3}]	1.495	1.462	1.457	1.546
Abs. coeff. [mm^{-1}]	0.750	0.734	0.731	0.748
Abs. correction	none	none	none	none
F(000)	1144	2288	2288	301
Total no. of reflections	29432	23519	60000	4750
max. 2θ [°]	28.28	28.27	28.21	25.9
Ranges (h, k, l)	$-15 \le h \le 15$	$-21 \le h \le 21$	$-17 \le h \le 17$	$-8 \le h \le 8$
	$-18 \le k \le 18$	$-17 \le k \le 12$	$-17 \le k \le 17$	$-10 \le k \le 10$
	$-23 \le l \le 21$	$-31 \le l \le 29$	$-38 \le l \le 35$	$-12 \le l \le 13$
Completeness to 2θ [%]	95.0	95.5	99.1	89.9
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11705/0/684	5991/0/339	12446/0/684	2221/0/187
Goof (F^2)	1.019	0.942	1.006	1.006
R indices [$I > 2\sigma(I)$]	0.0384	0.0323	0.0417	0.0254
R indices (all data)	0.0921	0.0632	0.0787	0.0616

round-bottomed flask, and toluene (20 mL) was added to it. The heterogeneous mixture was stirred at room temperature for 5 min followed by the addition of pyridine (0.158 g, 2 mmol). The blue supernatant liquid turned pink. The residue was filtered off, and the pink filtrate was left undisturbed. Pink crystals were collected after 3 d and dried in air. Yield: 34% (based on Co). IR (KBr): $\tilde{\nu}$ = 3412 (b), 3076 (ms), 1636 (s), 1603 (ms), 1531 (s), 1447 (ms), 1395 (s), 1218 (ms), 1154 (ms), 1040 (ms), 821 (s), 735 (s), 700 (s) cm^{-1}. Magnetic moment: 6.56 BM at 25 °C. UV/Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 521 nm (39.23).

Synthesis of IV: 2-Nitrobenzoic acid (0.34 g, 2 mmol) was dissolved in methanol (20 mL), and to this solution, sodium hydroxide (0.08 g, 2 mmol) was added. After 10 min of stirring, cobalt(II) sulfate heptahydrate (0.281 g, 1 mmol) was added to the solution, and the heterogeneous mixture was stirred for 30 min. To this heterogeneous mass, pyridine (0.15 g, 2 mmol) was added, and the mixture stirred for 10 min. The residue was filtered and discarded. Orange crystals were collected after 4 d from the filtrate. The crystals were collected and dried in air. Yield: 51% (based on Co). μ_{eff} = 3.952 BM at 25 °C. IR (KBr): $\tilde{\nu}$ = 3414 (wb), 3064 (w), 1604 (m), 1582 (s), 1555 (s), 1526 (s), 1484 (m), 1448 (s), 1400 (s), 1356 (s), 1303 (w), 1069 (w), 1041 (w), 911 (wb), 818 (s), 759 (w), 738 (s), 695 (s) cm^{-1}. UV/Vis (methanol): λ_{max} (ε, $M^{-1}cm^{-1}$)= 515 nm (6.7).

Supporting Information (see footnote on the first page of this article): The X-ray powder diffraction pattern of polymorphs **I**–**III** and the solid-state FTIR spectra of the polymorphs **I**–**III** are given.

Acknowledgments

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[1] a) I. Weissbuch, M. Lahav, L. Leiserowitz, *Cryst. Growth Des.* **2003**, *3*, 125–150; b) J. A. R. P. Sarma, G. R. Desiraju in *Crystal Engineering: The Design and Application of Functional Solids* (Eds.: K. R. Seddon, M. J. Zaworotko), Kluwer, Dordrecht, **1999**, vol. 539, pp. 325–356; c) J. Bernstein in *Polymorphism in Molecular Crystals*, Oxford University Press, **2002**; d) N. Blagden, R. J. Davey, *Cryst. Growth Des.* **2003**, *3*, 873–885.

[2] a) A. Dey, G. R. Desiraju, *CrystEngComm* **2006**, 478–482; b) J. Bernstein, R. J. Davey, J.-O. Henck, *Angew. Chem. Int. Ed.* **1999**, *38*, 3440–3461; c) G. S. McGrady, M. Odlyha, P. D. Prince, J. W. Steed, *CrystEngComm* **2002**, 271–276; d) R. J. Sarma, J. B. Baruah, *Chem. Eur. J.* **2006**, *12*, 4994–5000; e) R. J. Davey, N. Blagden, G. D. Potts, R. Docherty, *J. Am. Chem. Soc.* **1997**, *119*, 1767–1772.

[3] a) O. Almarsson, M. J. Zaworotko, *Chem. Commun.* **2004**, 1889–1894; b) T. Beyer, G. M. Day, S. L. Price, *J. Am. Chem. Soc.* **2001**, *123*, 5086–5094.

[4] a) C. M. Reddy, S. Basavoju, G. R. Desiraju, *Chem. Commun.* **2005**, 2439–2441; b) J. A. McMahon, M. J. Zaworotko, J. F. Remenar, *Chem. Commun.* **2004**, 278–279; c) A. V. Trask, N. Shan, W. D. S. Motherwell, W. Jones, S. Feng, R. B. H. Tan, K. J. Carpenter, *Chem. Commun.* **2005**, 880–882.

[5] a) F. Calderazzo, L. Labella, F. Marchetti, *J. Chem. Soc., Dalton Trans.* **1998**, 1485–1490; b) D. Braga, G. Cojazzi, A. Abati, L. Maini, M. Polito, L. Scaccianoce, F. Grepioni, *J. Chem. Soc., Dalton Trans.* **2000**, 3969–3975.

[6] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; b) K. M. Fromm, J. L. S. Doimeadios, A. Y. Robin, *Chem. Commun.* **2005**, 4548–4550; c) D. Braga, F. Grepioni, *Chem. Commun.* **2005**, 3635–3645; d) K. M. Fromm, E. D. Gueneau, A. Y. Robin, W. Maudez, J. Sague, B. Remi, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1725–1740; e) J. A. Bis, P. Visheshwar, R. A. Middleton, M. J. Zaworotoko, *Cryst. Growth Des.* **2006**, *6*, 1048–1053; f) D. Barga, F. Grepioni, S. Ellena, R. Gobetto, *Organometallics* **2006**, *25*, 4627–4633.

[7] a) R. C. Holz, *Coord. Chem. Rev.* **2002**, *232*, 5–26; b) D. Lee, P.-L. Hung, B. Spingler, S. J. Lippard, *Inorg. Chem.* **2002**, *41*, 521–531; c) D. E. Wilcox, *Chem. Rev.* **1996**, *96*, 2435–2458.

[8] a) L. Yu, G. A. Stephenson, C. A. Mitchell, C. A. Bunnell, S. V. Snorek, J. J. Bowyer, T. B. Borchardt, J. G. Stowell, S. R. Byrn, *J. Am. Chem. Soc.* **2000**, *122*, 585–591; b) P. E. Eaton, K. Pramod, T. Emrick, R. Gilardi, *J. Am. Chem. Soc.* **1999**, *121*, 4111–4123.

[9] a) A. Karmakar, R. J. Sarma, J. B.Baruah, *Polyhedron*, in press; b) A. Karmakar, K. Deka, R. J. Sarma, J. B. Baruah, *Inorg. Chem. Commun.* **2006**, *9*, 836–838.

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